

Carbon chemistry in a landfill leachate plume: hydrochemical modeling using ^{13}C isotopes

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Introduction

Pollution of groundwater has been observed world-wide at many old landfills constructed before the eighties as most lack leachate collection systems or liners preventing the migration of leachate to underlying aquifers. As conventional remediation techniques are not cost-effective, much research has been performed in the last decade to the performance of natural degradation processes leading to natural attenuation of pollution.

Since 1998 research to natural attenuation processes has been going on at the Banisveld landfill site, Boxtel, the Netherlands. Inside the plume degradation of DOC and apparently BTEX is coupled to reduction of iron-oxides, while at the top fringes of the plume nitrate is likely to be the preferential electron-acceptor. Microbial communities inside the plume are clearly different from non-polluted groundwater communities as observed by physiological profiling (Röling et al, 2000) and molecular genetic techniques (Röling et al, 2001). Microbial and geochemical processes have been modelled in a reactive transport model (van Breukelen and Griffioen, 2000) using PHREEQC 2 (Parkhurst and Appelo, 1999).

For evaluation of natural attenuation an array of techniques is often applied. Natural isotopes however are rarely chosen, although this group of parameters has good potential for indicating and quantifying the occurrence of degradation, redox-processes, dilution, and groundwater age dating. Therefore a research project was started in May 2000 to study the applications of natural isotopes in soil pollution research (Volkerink et al., 2000). Besides the landfill an industrial site polluted with benzene/ethylbenzene was chosen to study degradation of these chemicals using compound-specific ^{13}C and ^2H isotopes (Jonker et al., 2001).

In this paper the results of isotope analysis at the landfill site will be discussed. The following isotopes were measured: $\delta^{13}\text{C}$ and ^2H of dissolved methane to evaluate origin and processes governing the fate of methane in the plume; $\delta^{34}\text{S}$ of sulfate to evaluate possible sulfate-reduction next to iron-reduction in the plume; and $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) as parameters for geochemical modelling.

Methane

$\delta^2\text{H}$ and $\delta^{13}\text{C}$ of dissolved methane were measured for 9 samples along a central flow path in the flow direction of the plume, for one sample below, and for one sample above the plume. Methane isotopes inside the plume were characteristic of landfill gas and acetate fermentation ($\delta^{13}\text{C}\text{-CH}_4$: $-53.3 \pm 0.5\text{‰}$; $\delta^2\text{H}\text{-CH}_4$: $-304 \pm 6\text{‰}$), while the methane found below the plume was apparently formed by the CO_2 -reduction pathway (Hackley et al., 1996). Methane measured above the plume was lower in concentration and slightly enriched in ^{13}C (-50.3‰) with respect to landfill leachate methane. This indicates methane oxidation at the fringes of the plume under nitrate-reducing or sub-oxic conditions, as $\delta^{15}\text{N}\text{-NO}_3$ determined from the same sample was very positive ($+41.5\text{‰}$, 12 mg/L). The suspected denitrification coupled to

methane and possibly ammonium, Fe^{2+} and DOC oxidation will be verified by additional isotope analyses of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate, $\delta^{15}\text{N}$ of ammonium, and $\delta^{13}\text{C}$ of methane and DIC.

In the flow direction of the plume a weak correlation was found ($R^2 = 0.53$) between decreasing methane concentrations and slightly increasing $\delta^{13}\text{C}$ values. The calculated fractionation factor was very low ($\alpha \sim 1.001$) and may be indicative of degassing (Bergamaschi et al., 1997), which is supported by modeling results (van Breukelen et al. in prep.). For $\delta^2\text{H}-\text{CH}_4$ however no correlation was found.

Sulfate

Sulfate concentrations in the plume did not decrease in downstream direction indicating absence of sulfate-reduction. However the concentration pattern was irregular: high concentrations (max. 125 mg/L) were found up to three months after placement of the observation wells, while concentrations were much lower 16 months later (< 10 mg/L). From the last series of samples ^{34}S from sulfate was analysed: 5 samples from plume (3-10 mg/L), one above plume (54 mg/L), one below plume (1.7 mg/L). The samples showed low ^{34}S values and inverse correlation with concentration. The data fitted well on a mixing line (Fig. 1), while the calculated enrichment factor for possible sulfate-reduction was very low ($\epsilon \sim 3.4\text{‰}$; Fig. 2) with respect to values reported in literature ($\epsilon = 10\text{‰}$ ($\alpha = 1.010$) to 24‰ and higher; Krouse and Mayer, 2000). Including only plume samples while omitting the one with highest concentration yielded a value of 7‰ ($n=4$). Sulfate-reduction therefore is not likely, while probably oxidation of pyrite ($\delta^{34}\text{S}-\text{FeS}_2 \sim -2.5\text{‰}$) must have been occurred during installation of the observation wells. So, real sulfate concentrations in the plume must even be lower making sulfate-reduction an insignificant degradation process inside the plume.

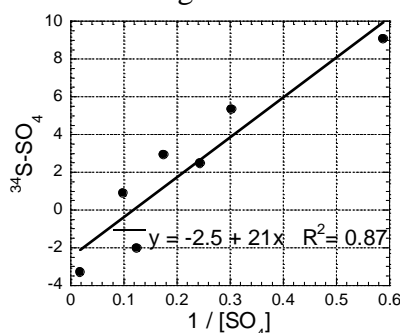


Figure 1. Mixing line

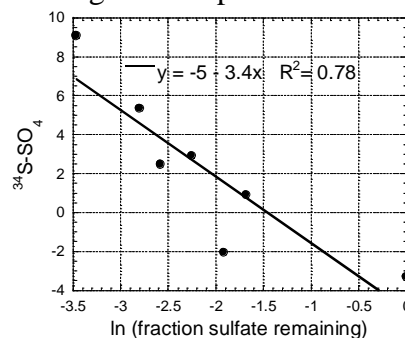


Figure 2. Calculation fractionation factor

Geochemical modelling of $\delta^{13}\text{C}$ in leachate plume

A forward reactive transport model has been made of the plume previously (van Breukelen and Griffioen, 2000) using PHREEQC2 (Parkhurst and Appelo, 1999). Degradation of DOC coupled to iron-reduction, cation-exchange of potassium and ammonium from the leachate in release for Fe^{2+} , Ca^{2+} and protons from the soil, and precipitation of carbonate minerals, especially siderite, were the dominant processes explaining observed water quality changes in downstream direction. Chloride concentrations indicated absence of dilution along the central flow path. Precipitation of Fe/Ca/Mg-carbonates appeared to be an important process, but unfortunately low amounts (modelled: < 1 mg/g) of precipitated carbonates in the initially carbonate free aquifer could not be determined. As precipitation of carbonates involves fractionation of $\delta^{13}\text{C}$, additional proof was tried to find by constraining the geochemical model to $\delta^{13}\text{C}$ values of methane ($\sim -53\text{‰}$, Δ (decrease in concentration along flow path) -0.5 mM), DOC ($\sim -27\text{‰}$, $\Delta -3.8$ mM) and DIC (decreasing from $+13.1\text{‰}$ to $+9.6\text{‰}$, $\Delta -35$ mM). The high $\delta^{13}\text{C}$ -DIC values are typical for landfill leachate (Hackley et al., 1996).

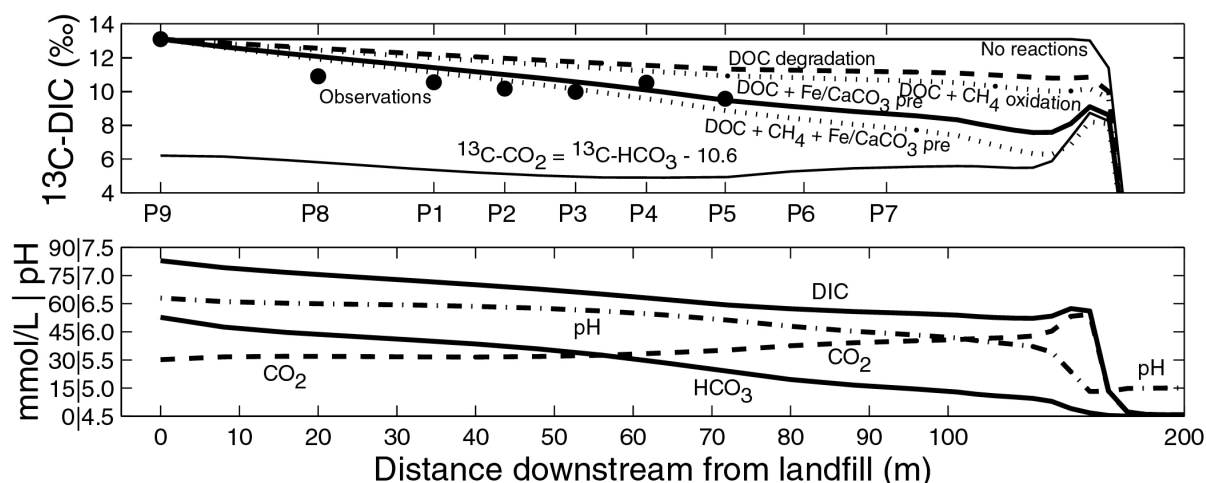


Figure 3. Results of forward reactive transport model of flow path in central part leachate plume. In upper figure the $\delta^{13}\text{C}$ -DIC values for several scenario's are shown, as well the $\delta^{13}\text{C}$ - CO_2 of the model including DOC degradation and calcite/siderite precipitation. Observations (wells p9-p5) are plotted by black dots. In lower figure the modeled concentrations of DIC, CO_2 , HCO_3^- and pH are shown.

$\delta^{13}\text{C}$ isotopic calculations were performed in the same PHREEQC 2 model by modelling ^{12}C and ^{13}C as separate solutes. ^{13}C of precipitating carbonate minerals was determined at each time step and distance by calculating the ^{13}C of bicarbonate and adopting a fractionation factor ($^{13}\epsilon_{\text{carbonate minerals - bicarbonate}}$) of +0.15‰ relative to this species.

The pH of the leachate plume is below neutral and decreases downstream from 6.6 to 5.9, while DIC decreases as well by precipitation of carbonates (Fig. 3). The effect of oxidation of DOC by iron-reduction lowers $\delta^{13}\text{C}$ -DIC only slightly (Fig. 3). Methane concentration decreases slightly downstream. Anaerobic oxidation of methane is unlikely based on hydrogen gas measurements, while the geochemical model indicated degassing of methane caused by rising pCO_2 pressures (Fig. 3) as a probable process. Also when both DOC and methane are assumed to be oxidised, simulated $\delta^{13}\text{C}$ -DIC values are too high. However when both DOC oxidation and fractionation caused by carbonate mineral precipitation are modelled, field observations are quite well simulated. The modelled $\delta^{13}\text{C}$ of precipitated carbonate minerals varied between 16.1‰-17.1‰.

References:

- Bergamaschi, P., 1997, *Journal of Geophysical Research-Atmospheres*. 102 (D21): 25383-25393
- Hackley, K.C., Liu, C.L. and Coleman, D.D., 1996, *Groundwater*. 34: 827-836
- Jonker, H., van Breukelen, B.M., Meijer, H.A.J., Mancini, S.A., Sherwood Lollar, B., Volkering, F., Groen, J., 2001, this proceedings
- Krouse, H.R. and Mayer, B., 2000, in *Environmental tracers in subsurface hydrology*, P. Cook, L. Herczeg, Eds. (Kluwer Academic Publishers, Boston): 195-231
- Parkhurst, D.L. and Appelo, C.A.J., 1999, U.S. Geol. Surv. Water-Resources Investigations Report 99-4259
- Röling, W.F.M., van Breukelen, B.M., Braster, M. and van Verseveld, H.W., 2000, *Water Sci. Technol.* 41: 47-53
- Röling, W.F.M., van Breukelen, B.M., Braster, M., Bin, L. and van Verseveld, H.W., 2001, submitted to AEM
- van Breukelen, B.M. and Griffioen, J., 2000, *Proceedings of the international conference on groundwater research, Groundwater 2000, Copenhagen, Denmark*: 315-316
- Volkering, F., van Breukelen, B.M., Groen, J., Meijer, H.A.J., Ahad, J.M.E., Sherwood-Lollar, B. and Kramers, J.D., 2000, *Proceedings of CONSOIL 2000, Leipzig, Germany*: 214-221 (Vol 1)